

Screening Air Samples for
Polynuclear Aromatic Compounds
A Field Study

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SCREENING AIR SAMPLES FOR POLYNUCLEAR AROMATIC
COMPOUNDS: A FIELD STUDY¹

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The use of simple and cost-effective luminescence techniques for screening air particulate samples is described. Two analytical methods, synchronous luminescence and room temperature phosphorescence, are employed to monitor the content of polynuclear aromatic species in air particulate extracts collected at a wood-burning community. The validity and efficacy of this cost-effective screening approach are demonstrated via comparison of the screening data with results obtained by detailed gas chromatography/mass spectrometry analysis.

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SCREENING AIR SAMPLES FOR POLYNUCLEAR AROMATIC COMPOUNDS: A FIELD STUDY

Introduction

Human exposure to PNA compounds present in the atmosphere is of concern because of the potential health hazards associated with many PNA species found to be carcinogenic in laboratory animal tests. Any comprehensive assessment of the potential health effects related to air pollution requires a long-term monitoring and analysis program designed to handle large numbers of air samples.

Detailed characterization of complex environmental samples can be conducted using analytical techniques such as high-performance liquid chromatography (HPLC)¹ or gas chromatography/mass spectrometry (GC/MS).² These analytical techniques, however, cannot be employed on a routine and systematic basis to study all samples due to the high cost involved. It is often desirable to have a screening procedure to prioritize these samples before a detailed analysis is conducted on a subset of samples to reduce the total cost of monitoring programs and environmental assessment studies.

This comparative study evaluated the efficacy of two simple and rapid analytical techniques, e.g., synchronous luminescence (SL) and room temperature phosphorescence (RTP), for routine screening of samples for polynuclear aromatic (PNA) content. The SL and RTP techniques were used to monitor PNA compounds in outdoor ambient air samples collected in one wood-burning residential area. The luminescence screening procedures conducted at Oak Ridge National Laboratory ranked all samples on the basis of their PNA content. The efficacy of the screening procedure was evaluated by comparing the SL and RTP results with data obtained from independent GC/MS analyses performed by PEDCo Environmental, Inc. The results of this field evaluation showed that the luminescence screening procedure constituted an effective tool for ranking air samples for their PNA content and could serve to reduce the number of GC/MS analyses needed to characterize PNA compounds in ambient air.

Experimental Methods

The Luminescence Techniques

The screening procedure evaluated in this research project is based upon two simple luminescence techniques, room temperature phosphorescence (RTP) and synchronous luminescence (SL) spectroscopy.

Synchronous Luminescence. The theory and rationale behind the SL methodology have been described previously in detail.^{3,5} Only the major features of this technique are given here. Conventional luminescence spectroscopy utilizes either a fixed emission or excitation wavelength. With synchronous excitation spectroscopy, the luminescence signal is

recorded while both emission and excitation monochromators are simultaneously scanned; the wavelength interval, $\Delta\lambda$, between the two monochromators is kept constant throughout the measurement. Improved selectivity without loss of simplicity in experimental protocol is the main advantage of this method. In general, the spectral structure of the composite mixture is more resolved because the spectra of the individual components are simplified and the bandwidth narrowed.⁴ The decrease of spectral overlap from various components in the mixture is another attribute of the synchronous technique.

The concept of synchronous excitation can be applied both to fluorescence, e.g., synchronous fluorimetry (SF), and to phosphorescence, e.g., synchronous phosphorimetry (SP). In the case of SF, the Stokes shift, e.g., the wavelength difference between the 0-0 bands in emission and absorption, determines the optimum value of $\Delta\lambda$ which is often set at 3 nm. For SP it is the singlet-triplet energy difference that determines the optimum value of $\Delta\lambda$.⁶ In this work, the screening involved only SF measurements.

A noteworthy attribute of the synchronous technique is the simplicity of instrumentation. The technique often requires no additional equipment other than an inexpensive switch for most available spectrometers currently used in conventional fixed-excitation measurements. Several instruments with interlocking capability of two monochromators as a standard feature are commercially available.

Room Temperature Phosphorimetry. The phosphorescence signal of PNA compounds in solution or in the gas phase is extremely weak at ambient temperatures. Due to its long lifetime (10^{-3} seconds to several seconds) the phosphorescence emission is completely quenched by collisions with surrounding molecules present in solutions or in the air. Intramolecular vibrational and rotational deactivation processes are also possible phosphorescence quenching mechanisms. Therefore, conventional phosphorimetry requires the use of low-temperature matrices that serve to reduce the collisional quenching mechanisms and radiationless deactivation processes. Due to the requirement of cryogenic equipment and refrigerant, conventional phosphorimetry has limited usefulness for routine applications or field measurements.

Unlike conventional phosphorimetry, RTP is a technique based on the phosphorescence from organic compounds adsorbed on solid substrates at room temperature. It has been shown that the adsorbed state of the analyte molecule on the solid substrate resulted in increased molecular rigidity, thus reducing collisional and rotational deactivation. Although a variety of solid substrates such as silica, alumina, paper, and asbestos can be utilized, filter paper is normally used because of its convenience and low cost. Unlike conventional phosphorimetry, the RTP technique does not require cryogenic equipment - a definite advantage for routine field measurements.

Screening Protocol

The full details of the protocol for screening procedures are described elsewhere.⁷ The four major steps involved in the protocol are: 1) serial dilution of the sample extracts, 2) SF measurement, 3) RTP measurement, and 4) ranking the samples. The experimental conditions are as follows:

Serial dilution:

samples diluted 10-, 50-, and 250-fold in ethanol.

SF measurement:

wavelength interval $\Delta\lambda = 3$ nm
spectrometer bandpass = 1.5 nm
spectral range: 260 - 500 nm
scan speed: 120 nm per minute
total scan time = 2 minutes

RTP measurement:

fixed-excitation at 290 nm, 343 nm, and 390 nm
spectrometer bandpass = 5 nm
spectral range = 400 - 700 nm
scan speed = 120 nm per minute
total scan time = 2.5 minutes

A simple computer program was developed to calculate a ranking index for SL and RTP screening. This program receives as inputs the peak height intensities of a previously determined number of emission bands, the sensitivity factor of the detector, the dilution factor of the sample, and the peak height of a given band of a known reference standard sample. These peak height intensities are then corrected to the reference standard, normalized to the unity sensitivity scale of the spectrometer, and original dilution (1:1) of the sample, and summed over the sample being monitored. The summed value of the peak height for each sample is stored in a one-dimensional array and used as a basis for ranking. Because most of the PNA compounds fluoresce and/or phosphoresce, the rationale of this ranking protocol is based upon the idea that the higher the total peak height of the SL and RTP bands, the more concentrated the samples are in PNA species.

Results and Discussion

The SF and RTP were conducted on a synthetic mixture of PNA compounds. This reference standard mixture was prepared by PEDCo Environmental, Inc., and contained known concentrations of 10 commonly encountered PNA compounds. The screening procedures were first tested on this mixture to investigate possible spectral interferences and concentration effects. Figure 1 illustrates an example of RTP spectra that shows the characteristic peaks for triphenylene (TRIP), phenanthrene (PHEN), pyrene (PYR), chrysene (CHRY), fluoranthene (FLUOR), benz[a]anthracene (BAA), and benzo[e]pyrene (BEP). These compounds were identified in the standard mixture by RTP using various

fixed excitation wavelengths at 290 nm (Figure 1a), 315 nm (Figure 1b), 330 nm (Figure 1c), and 343 nm (Figure 1d). Other PNA compounds, such as anthracene, benzo[a]pyrene, perylene, and benzo[k]fluoranthene could be characterized by synchronous fluorescence measurements.

In the air particulate studies the SF and RTP screening procedures have been evaluated on a variety of air samples during an extensive comparative study at Oak Ridge National Laboratory (ORNL) and in laboratories of other Environmental Protection Agency (EPA) contractors. Over fifty field samples were collected in two studies on exposure assessment in two wood-burning communities at Waterbury, Vermont, and Petersville, Alabama, respectively. This communication discussed the results for a series of ten field samples collected by a Tennessee Valley Authority (TVA) sampling team at the Petersville community. These samples were extracted in cyclohexane, concentrated, sealed in glass vials, and sent by PEDCo to ORNL for luminescence screening.

RTP and SF measurements were conducted directly with the cyclohexane extracted samples further diluted in ethanol without any chemical fractionation procedure. The RTP spectra of the air sample extracts generally exhibited a broad-band structure with the emission between 500 nm and 600 nm. The average intensity of the peak height of the RTP spectra obtained with ~~8~~ different excitation wavelengths (290, 343, and 390 nm) was used as a basis for ranking. These ~~three~~ wavelengths were selected to excite various PNA species having more than three rings. The diffuse spectral structure of the RTP emission is an indication of the complex nature of the field samples with no dominant presence of a specific compound or group of compounds.

The SF profiles of the ten field samples and a blank are shown in Figures 2 and 3. The SF spectra show some structure with six major bands at about 316, 336, 360, 404, 434, and 472 nm. For comparison purposes all the spectra shown in these figures correspond to samples diluted to a same concentration (1:50 dilution). In the actual ranking process, data obtained with more concentrated solution were used for samples with low PNA content. Table 1 gives the results of the ranking procedure of the 10 field samples by SF and RTP screening. The SF ranking index is a relative number proportional to the total peak height of the main emission bands in the SF spectra obtained with $\Delta\lambda = 3$ nm. The six main SF emission peaks observed with these field samples were monitored at 316, 336, 360, 404, 434, and 472 nm. The RTP ranking proportional to the average peak height of RTP emission obtained with excitation at 290, 343, and 390 nm.

The field samples were independently analyzed by PEDCo using GC/MS for 10 specific PNA compounds, viz. phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, triphenylene, benzo[e]pyrene, benzo[a]pyrene, and perylene. Table 2 shows the comparison between the SF/RTP screening results and the data obtained by detailed GC/MS analysis. Considering the approximate nature of the screening procedures, the SF/RTP results are also in good agreement with

the GC/MS data. Examination of the SF profile of samples CG 642 and CG 635 in Figure 3 also indicates that the intensity distribution of the SF spectral profile exhibit a relatively higher emission for wavelengths >360 nm where the emission occurs for most of PNA compounds having more than 3 benzene rings. This spectral feature for samples CG 642 and CG 635 is further underscored in Figure 4 showing that the two SF bands at 404 and 434 nm are more intense than the bands located <360 nm. The GC/MS data on Table 2 for samples CG 642 and CG 635 are also in agreement with this qualitative prediction. The SF profile can therefore be used not only to provide an index for ranking but also to provide useful information about the ring size of the PNA constituents in the sample. Applications of this screening procedure to other air samples collected at different test sites have also been successful and are described in detail elsewhere.

Conclusion

The results of this study show that the SF/RTP procedures provide a simple and cost-effective tool to screen complex environmental samples for PNA species. Prior to this study, our goal was to develop a screening tool that can rank air samples on a scale (1, 10, 100, etc.). The field results obtained to date indicate that the screening process can provide a ranking capability suitable even for samples whose PNA content difference is less than one order of magnitude. Considering the approximate nature of the ranking process and the simplicity of the screening procedure, the agreement between the SL/RTP data and results obtained by more detailed GC/MS analyses is excellent. Further research and field evaluation of this screening technique would lead to the development of an effective analytical tool that can rapidly rank large numbers of environmental samples, reduce the number of GC/MS analyses, and decrease the cost of human exposure assessments and environmental impact studies.

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Table I. Results of the Ranking of Ten Field Samples by SF and RTP

Sample Number	Relative RTP Ranking Index ^a	Relative SF Ranking Index ^b
CG616	35	90
CG545	25	75
CG560	20	55
CG629	15	20
CG533	1	15
CG624	5	15
CG619	10	65
CG642	15	45
CG627	20	65
CG635	2	20

^aThe RTP ranking index is a relative number proportional to the average peak height of the RTP emission using three different excitation wavelengths at 290, 343, and 390 nm.

^bThe SF ranking index is a relative number proportional to the average peak height of the six major emission bands in the SF spectra using $\Delta\lambda = 3$ nm. For these air samples the emission bands were at 316, 336, 360, 404, 434, and 472 nm.

Table II. Comparison of the SF/RTP Screening Results
with GC/MS Data

Sample Number	PNA Content Ranking by SF/RTP ^a	Total Content for 10 PNA Compounds (GC/MS Data: $\mu\text{g/mL}$) ^b
CG616	125	2.118 ^c
CG545	100	2.264
CG627	85	1.119
CG560	75	1.278 ^c
CG619	75	1.094
CG642	60	2.665 ^{c,d}
CG629	35	0.203 ^c
CG635	22	0.414 ^d
CG624	20	0.134
CG533	16	0.260

^aThe combined SF/RTP ranking index is the sum of the SF and RTP indexes given in Table I. The measurements were conducted at the Oak Ridge National Laboratory.

^bThe GC/MS analyses were performed by PEDCo Environmental, Inc., for 10 PNA compounds (phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, triphenylene, benzo[e]pyrene, benzo[a]pyrene, and perylene).

^cAverage values of two replicate GC/MS analyses conducted in these samples.

^dSee discussion about samples CG 642 and CG 635 in text.

ROOM TEMPERATURE PHOSPHORESCENCE SPECTRA OF THE STANDARD REFERENCE MIXTURE

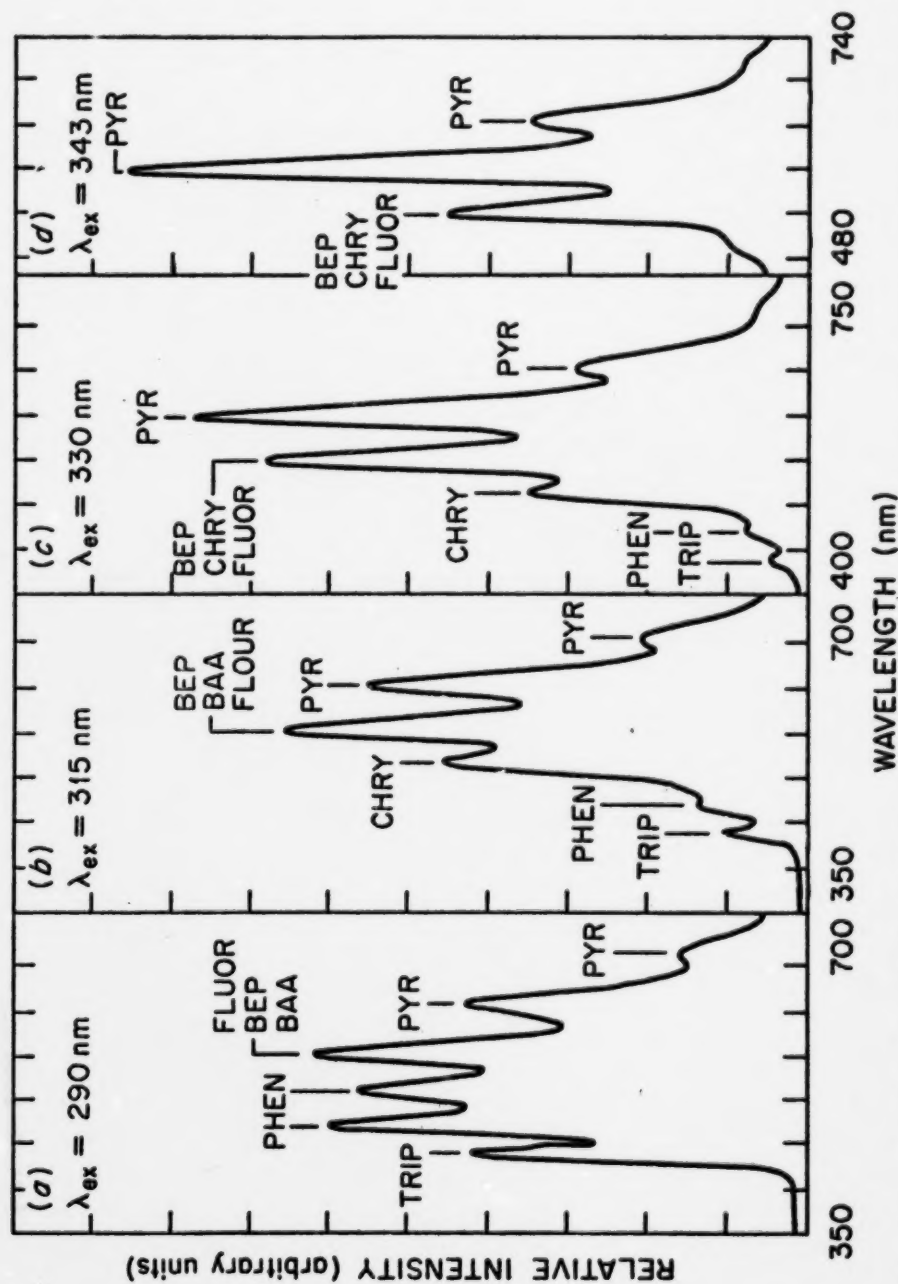


Figure 1: Room temperature phosphorescence spectra of the standard reference mixture using various excitation wavelengths. TRIP = triphenylene; PHEN = phenanthrene; FLUOR = fluoranthene; BEP = benzo[*e*]pyrene; BAA = benz[*a*]anthracene; PYR = pyrene; and CHRY = chrysene.

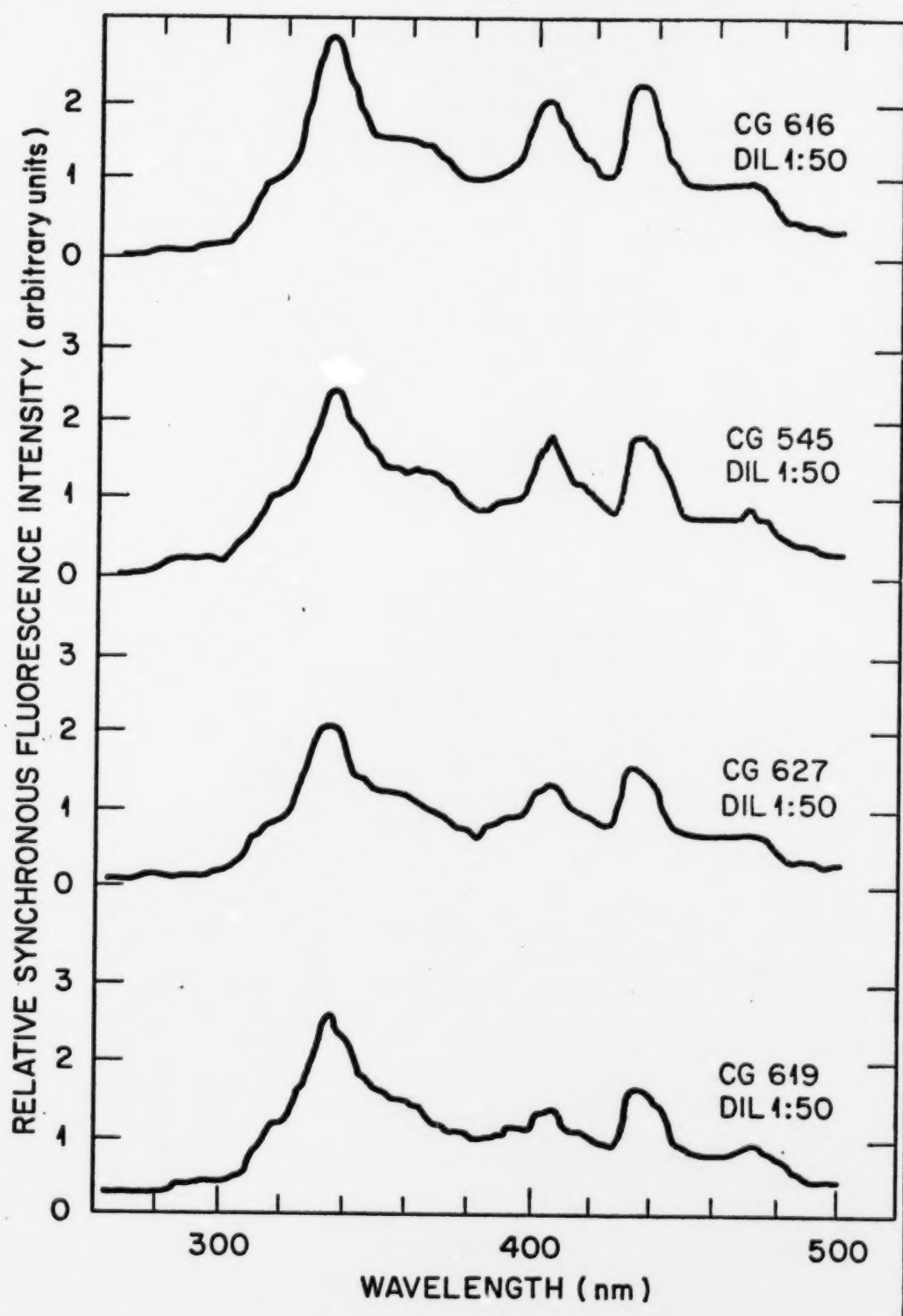


Figure 2: Synchronous fluorescence profiles of air samples extracts.

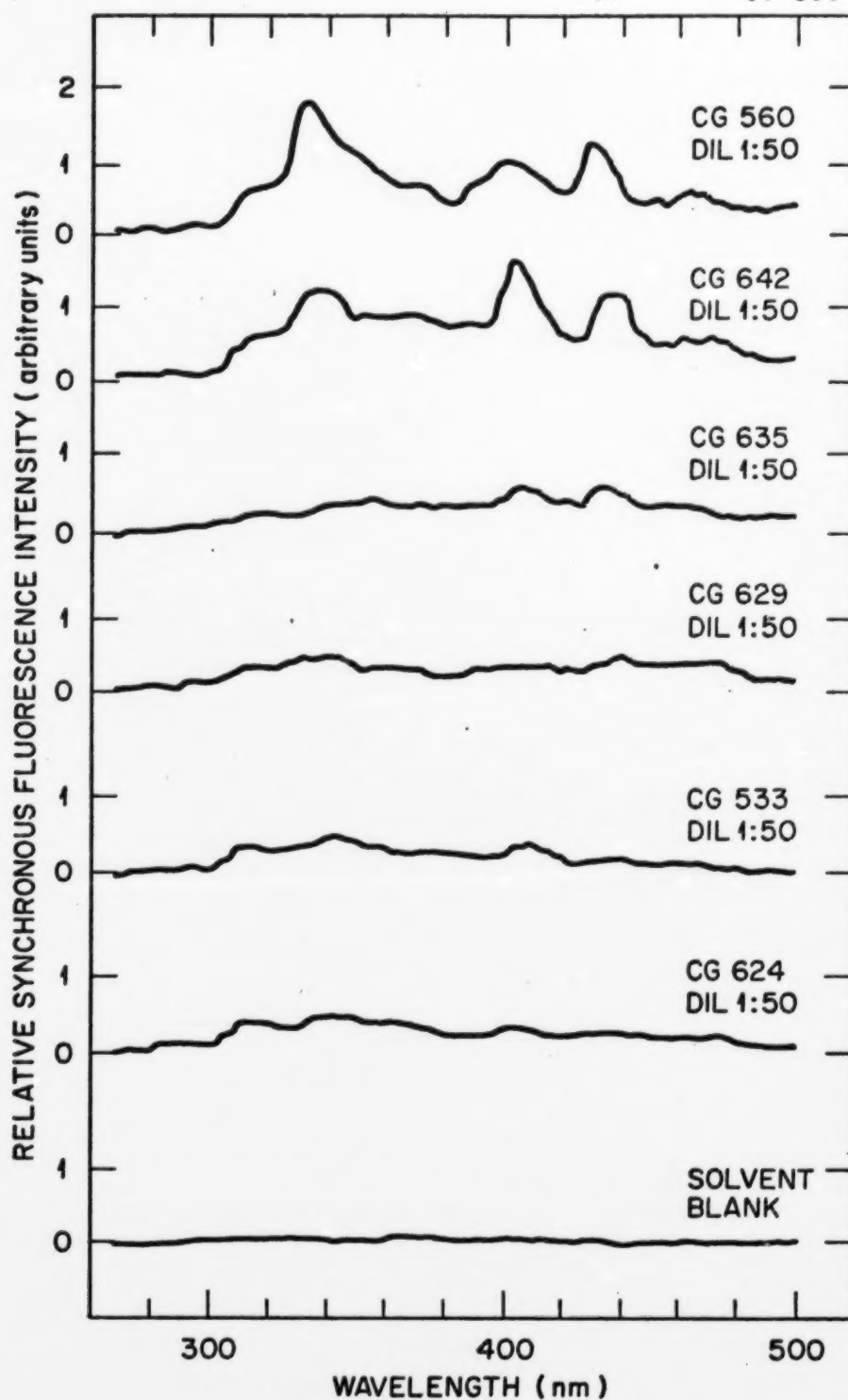


Figure 3: Synchronous fluorescence profiles of air samples extracts.

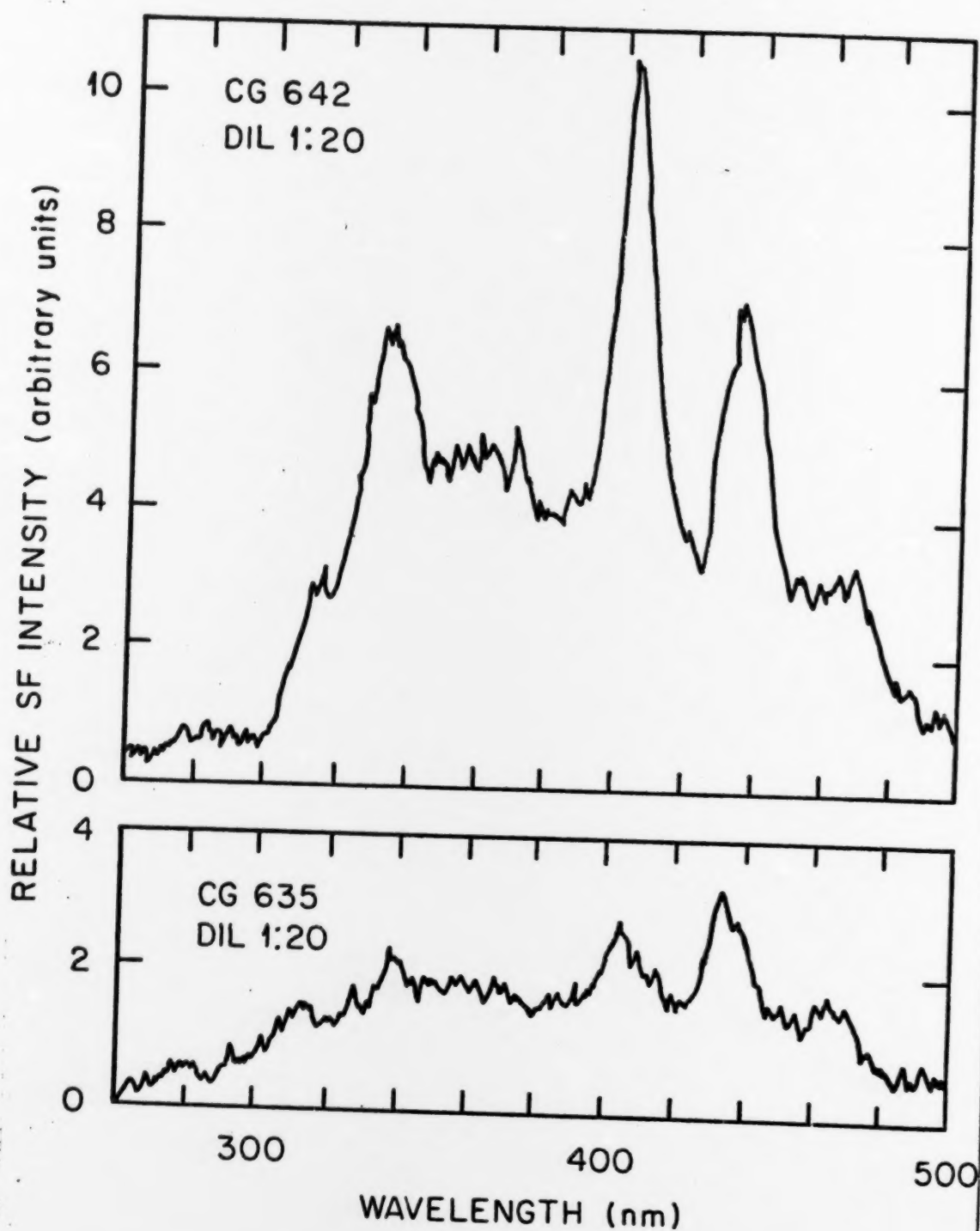


Figure 4: Synchronous fluorescence of two air sample extracts.